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STUDIES ON ENVIRONMENTAL POLLUTION BY MISSILE PROPELLANTS

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FEBRUARY 1969

20050211009

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AEROSPACE MEDICAL DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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800 - April 1969 - CO455 - 72-1608

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FOREWORD

This study was initiated by the Chemical Hazards Branch of the Aerospace Medical Research Laboratory, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. The research was performed in support of Project No. 6302, "Toxic Hazards of Propellants and Materials," Task No. 630204, "Environmental Pollution," under Contract No. AF33(615)-1767 with the Science Research Institute, Oregon State University, Corvallis, Oregon. Dr. C.H. Wang was the principal investigator for Oregon State University, and Dr. Sheldon A. London was contract monitor for the Aerospace Medical Research Laboratory. Research was initiated May 1964 and completed June 1967.

This technical report has been reviewed and is approved.

C.H. KRATOCHVIL, Colonel, USAF, MC
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ABSTRACT

The effects of single experimental exposures of plants, fish and microorganisms to members of a group of inorganic fluoride oxidizing agents have been summarized. The information obtained has enabled estimation of the damage to be expected as a result of single accidental exposures in the field. These agents--nitrogen trifluoride (NF_3), tetrafluorohydrazine (N_2F_4), oxygen difluoride (OF_2), chlorine trifluoride (ClF_3), bromine pentafluoride (BrF_5), and chlorine pentafluoride (ClF_5)--vary in chemical behavior and biological effects. NF_3 is relatively innocuous; OF_2 must be avoided absolutely by animals and plants, and both are quite stable chemically. The interhalogens react readily in contact with environmental constituents, and while destructive at the site of initial contact, they are self limiting in effect. N_2F_4 also reacts easily, but should cause only moderate damage. Plant injury in all cases would probably be limited to the currently growing crop, with little possibility of carry-over effects in soil.

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SECTION I

INTRODUCTION

This report is designed to assist in field evaluation of the effects of inorganic fluoride oxidizing agents accidentally released into the environment. The discussion, while general in nature, is based upon laboratory investigations of the biological effects of nitrogen trifluoride (NF_3), tetrafluorohydrazine (N_2F_4), oxygen difluoride (OF_2), chlorine trifluoride (ClF_3), bromine pentafluoride (BrF_5) and chlorine pentafluoride (ClF_5). Pertinent chemical and physical behavior of the agents have also been reviewed. The various characteristics of each compound provide a basis for predicting its effects and reactions in the environment and for developing means to attenuate its effects after release in the field.

The manner of employment of these compounds dictates that field contact will be of short duration, at concentrations varying from a few parts per million to several percent in the atmosphere, as distinguished from contact with industrial effluvia in which only a few parts per 10 billion may be present over long periods of time. Spillage of any of the agents discussed here, whether in production, transport, or use will result initially in exceedingly destructive concentrations of toxic materials. As the agents disperse and/or react in the atmosphere over a period of a few minutes or hours, they eventually become sufficiently dilute that biological effects are negligible. This report is concerned almost entirely with the effects of brief exposures to moderate concentrations of toxic materials, the situation expected over broad areas downwind of high density spillage.

The information in this report is derived primarily from research previously reported (ref. 1, 2). Where pertinent, reference is also made to studies of inorganic fluoride intoxication of mammals (ref. 3). The intoxication of nonmammalian air-breathing species by inorganic fluoride oxidizing agents has not been studied, nor have these investigations been extended to the higher forms, such as nematodes, inhabiting soil.

SECTION II

REVIEW OF CHEMICAL PROPERTIES

In evaluating the potential reactions of inorganic fluoride oxidizing agents with materials of construction and with inert factors of the environment, the basic general chemistry of the compounds should be considered.

Nitrogen trifluoride (NF_3)

Nitrogen trifluoride, although a strong oxidizing agent, is remarkably unreactive. It is not affected by dilute basic or acid solutions and it is reactive with water vapor only upon electrical sparking to produce such products as HF, NO and NO_2. If appropriate energy input is provided, gaseous NF_3 can also be made to react with a variety of gaseous reducing agents such as H_2S, NH_3 and various hydrocarbons. NF_3 is non-reactive with dry glass but it reacts readily with glass in the presence of water and therefore must be expected to similarly react with siliceous surface minerals. In the laboratory, modest amounts of NF_3 have been stored for long periods without reaction in a polyethylene bag. We have, however, also experienced spontaneous reaction of NF_3 with a relatively inert fluorocarbon.

Tetrafluorohydrazine (N_2F_4)

A characteristic of the chemical behavior of N_2F_4 is its existence in a dissociation equilibrium with the difluoroamino free radical: $N_2F_4 \rightleftharpoons 2NF_2\cdot$. The difluoroamino radical is capable of prolonged existence in the free state, a behavior similar to that of nitrogen dioxide. Most of the reactions in which N_2F_4 participates are probably reactions with the $NF_2\cdot$ free radical.

In air and water together, N_2F_4, unlike NF_3, is highly reactive at ambient temperatures and pressures. The parent compound probably disappears a short time following spillage if there is water in the air. The reaction proceeds through the formation of nitrosyl fluoride (NOF) and nitrogen dioxide (NO_2). Nitric oxide (NO) is also found and it slowly oxidizes further to NO_2. The degradation of N_2F_4 will not proceed in the presence of oxygen or water alone, but with both in adequate supply, N_2F_4 at a concentration of 1% will disappear in a matter of seconds.

Chlorine trifluoride (ClF_3)

Chlorine trifluoride is a nearly colorless gas which boils at 11.75°C; in cool temperatures, it may simply pool in the vicinity of spillage or may condense on objects of high heat capacity. It fails to react only with nitrogen and possibly platinum and polonium. It can cause immediate ignition of organic materials and will maintain combustion of metals once kindling temperature is achieved. The reaction of ClF_3 with water is explosive, unless the water is available in a finely divided form at a limited rate. Because of the relatively low vapor pressure of ClF_3 and its reactivity with water, the nature of its reaction products have yet to be satisfactorily identified. We have, however, found that most of the fluoride in such reaction mixtures is apparently in the form of hydrofluoric acid and that extensive quantities of oxidizing compounds are formed. These general reactions are true of each interhalogen. In spite of its reactivity, however, ClF_3 gas at ambient temperatures and at concentrations of 1,000 - 2,000 ppm will remain without reaction in contact with many organic materials, especially polyethylene.

Each of the interhalogens is soluble to some extent in organic materials such as neoprene or Kel-F oil. This is a source of some danger, since a surge of pressure or a blow upon the material may create a critical concentration and cause an explosion.

Bromine pentafluoride (BrF_5)

Bromine pentafluoride is similarly reactive with almost every known element and like ClF_3, attacks organic compounds vigorously. Because of its high boiling point of 40.8°C, it condenses at room temperature and in handling equipment will accumulate as a liquid at points of high heat capacity, resulting in extremely hazardous local concentrations of the agent.

Slow introduction of small amounts of liquid BrF_5 into liquid water produces a reaction so energetic that light is emitted as well as distinct explosive sounds.

Chlorine pentafluoride (ClF_5)

This compound behaves somewhat similarly to the other interhalogens especially in water, but is not so severely reactive. However, its capability for oxidizing organic material is such that it also must be handled with great care. Since it boils at -13.1°C, it too is capable of condensing from the atmosphere to form dangerous concentrations of liquid ClF_5.

Oxygen difluoride (OF_2)

OF_2 is a low boiling point compound which is toxic at extremely low levels, possibly below the odor threshold. It is soluble to the extent of about 6.7 milliliters of gas per 100 ml water at 0°C. It is also capable of slow reaction with water. It cannot be easily detonated or reacted by sparking, but will undergo thermal decomposition at temperatures above 250°C. The compound is relatively stable in contact with glass over long periods of time, although it can be decomposed slowly by light. Gaseous OF_2 can be safely mixed with hydrogen, methane and carbon monoxide, but with sparking, these mixtures will explode violently.

The relative insolubility of OF_2 in water eliminates much of its potential for damage to aquatic organisms, but since it is relatively stable, it does not readily react in the environment following spillage as should be expected of the interhalogens. The result is that toxic concentrations of this gas may remain in an area for very long periods of time.

SECTION III

BIOLOGICAL EFFECTS OF INORGANIC FLUORIDE OXIDIZING AGENTS, SODIUM FLUORIDE AND HYDROFLUORIC ACID

NF_3

Of the various inorganic fluoride oxidizing agents, NF_3 is the least dangerous to lower organisms. Because of its insolubility and high vapor pressure, it does not attack fish and other aquatic organisms. It is physically possible that a surface attraction between NF_3 and soils might bring the gas into contact with soil microorganisms, but in laboratory experiments, the bacteria have been found insensitive to high concentrations of the dry gas. Plants in direct contact with 1% NF_3 in air for 30 minutes have shown no detectable signs of damage. Seed germination was found to be barely inhibited after exposure to undiluted NF_3 for one hour, a condition which is highly unlikely to occur in the field. Toxicity to mammals is also minimal; a 1% NF_3 atmosphere is lethal only after about 1 hour of exposure. The effects upon mammals are apparently associated with a specific oxidation of hemoglobin to methemoglobin, which is incapable of oxygen transport.

N_2F_4

Tetrafluorohydrazine is only slightly more toxic than nitrogen trifluoride. It is similar to NF_3 in having a low boiling point and low solubility which decreases its capability to attack aquatic organisms. Limited effects of N_2F_4 upon plants can be detected after a prolonged exposure to 1,000 ppm of the gas in air, and it is lethal to mammals after 30 minutes of exposure to a concentration of 10,000 ppm in air.

It is difficult to maintain an intact experimental atmosphere of N_2F_4 in the laboratory because of the reactivity of the compound in the presence of water and air. In the field, these decomposition reactions should also proceed very rapidly, particularly if humidity is high. In the event of N_2F_4 spillage, the problems to be overcome would probably relate primarily to the effects of nitric oxide and nitrogen dioxide in the atmosphere, and some HF accumulation in surface water.

OF_2

The two low-boiling-point compounds discussed above have features which diminish their potential effect upon the organisms they contact. There are no such advantages in the case of OF_2. As a gas, it will tend to disperse rapidly, but because of the very high toxicity to plants and mammals, this characteristic merely adds to its destructive effect. The solubility of OF_2 is sufficiently limited so that it has no effect upon fish under field conditions, although when confined over an aquarium, the gas reacts with water to eventually form enough HF for lethal activity. Such solutions also have a definite oxidizing capability which disappears when the gas is removed.

Visible changes in growth rate of some plants may follow contact with as little as 1.5 ppm OF_2 for a 30-minute period. Squash plants are particularly sensitive and demonstrate a marked increase in stem length during the several days following exposure. Appreciable surface effects are not grossly visible after such a low exposure of OF_2, but at concentrations higher than 3 ppm OF_2, there is loss of pigmentation and an apparent physiological dessication which seems not to be a result of direct reaction between the toxic gas and the surface of the plant, but rather a metabolic disturbance resulting in failure of maintenance of the surface of the plant. These symptoms have appeared in all of the species examined. Many of the manifestations of OF_2 toxicity to plants do not appear until several hours after exposure, which also suggests the possibility of metabolic disturbance rather than a direct superficial reaction of the agent with the structure of the plant. However, at OF_2 concentrations of 100 ppm or more, the tip burn and bleaching appear quickly and are probably caused by contact reactions.

OF_2 is highly toxic to mammals and presumably to other air-breathing organisms. Lethal effect may follow a 10-minute exposure to 15-ppm of OF_2 in air. Death following such an exposure is usually delayed 20 - 40 hours following contact, and is associated with a slowly developing failure and destruction of pulmonary cells.

The Interhalogens

The interhalogens may be expected to attack a much broader spectrum of organisms than any of the other gases. Each gas of this group has a relatively high boiling point and each reacts readily with water. The acid and oxidizing products which are known to result from reactions with water may be expected to attack aquatic species, and the parent gases are directly corrosive to plant or animal tissues.

The first effects of severe exposure of fish to solutions of each of the compounds is loss of large amounts of surface mucus and emptying of the digestive tract. These effects are by no means specific, however, and can result from a variety of intoxicants. At fluoride concentrations of 22.5 µg per ml or greater, ClF_3, ClF_5, and BrF_5 solutions are each lethal to goldfish within about one hour after the beginning of a continuous exposure (Table I). Lower concentrations require longer exposure for lethal effect. At a concentration of 5 µg of fluoride per ml, ClF_3 solutions were lethal to fish after 2 - 5 hours of contact. Similarly, the minimal lethal fluoride concentration for solutions of BrF_5 was between 6 and 8 µg per ml and that for ClF_5 was found to be between 5 and 7 µg per ml. Below these concentrations, no appreciable effects appear regardless of the duration of exposure. This information is based upon experiments in aquaria of finite size, however, and in bodies of water with low fish population. The minimal toxic concentration probably would be decreased in larger bodies of water with greater absolute amounts of toxic materials, and increased in the presence of large numbers of fish.

If the pH of a ClF_3 solution is elevated to 6.5, and sufficient cysteine is added as a reducing agent, the solution will be essentially non-toxic. Neither treatment alone decreases the toxicity of ClF_3 in solution. Each procedure by itself results in some attentuation of the lethal effect of ClF_5 solutions, however, and the lethal effects of BrF_5 solutions are completely lost after neutralization of the pH to 6.5. The oxidizing components in BrF_5 solutions have not been found toxic to fish.

These particular attenuation effects can be demonstrated at increasing interhalogen concentrations until the toxicity of added cysteine or fluoride salts supervenes. It is apparent that intoxication induced by fluoride salts plays nc part in the activity of water solutions of interhalogens. Sodium fluoride at concentrations as high as 500 µg fluoride per ml is lethal to only about 50% of fish exposed over a period of 24 hours. Solutions containing 100 µg fluoride per ml as sodium fluoride caused no visible changes to fish in 48 hours of continuous exposure. It is, therefore, probable that appropriate application of alkaline reagents in the field should limit the toxic activity of interhalogen solutions draining into relatively static ponds or sloughs.

TABLE I. Survival Time of Goldfish Lethally Exposed to Several Concentrations of Interhalogens and HF in Aqueous Solution

Treatment	Concentration $\mu g\ F^{-}/ml$	Average Survival Time (Minutes)	Range of Survival Times
ClF_3	22.5	47	(40 - 69)
"	15	66	(60 - 91)
"	10	101	(50 - 119)
"	5	--	(120 - 300)
ClF_5	22.5	32	(23 - 50)
"	15	57	(28 - 90)
"	10	140	(60 - 240)
"	6.6		no effect
BrF_5	22.5	63	(51 - 70)
"	15	all died between 2 and 9 hours	
"	10		no effect
HF	20	360	(3.5- 9)
"	30	80	(70 - 100)
"	40	50	(35 - 75)

The pH related toxicity of interhalogen solutions is probably almost entirely due to HF, since the toxicity of HF solutions is comparable to that of ClF_3 and BrF_5 solutions. In addition, other inorganic acids are less toxic than HF when compared on the basis of pH and are more easily neutralized by fish. At a pH of 3.9, three liters of dilute hydrochloric acid, a strong acid, was found to cause no lethality to a group of 10 goldfish during the first 24 hours of exposure. During this time, pH was elevated by the fish to 5.65 and during the subsequent 48 hours, pH was raised to 6.7. Two fish died during this period, but the pH change from 3.9 to 6.7 was accomplished by 10 fish with a total weight of less than 30 grams. Goldfish have a similar capability for neutralization of nitric acid solutions. Exposures of groups of fish to 3 liter volumes of either HCl or HNO_3 at a pH of 3.5 or below resulted in 100% lethality within 2 hours, with little or no change in pH.

In a comparable experiment, three liters of hydrofluoric acid at pH 3.9 was lethal to all 10 goldfish in 4 hours of exposure, and the pH of the solution was raised by the fish from 3.9 to only 4.1. With 10 new fish placed in the same solution, it took about 2 hours to raise the pH further to 4.35 and 24 hours to achieve a pH of 5.9. Four of the second group of fish died during this period. The survivors were replaced in the solution with 10 new fish and the pH was raised by these fish to 6.8 in 48 additional hours with no fatality. This experiment perhaps illustrates a basic difference in the activity of highly ionized and partially ionized intoxicants. Solutions of HF, a weak acid, contain a substantial proportion of non-ionized HF which is able to penetrate cell membranes where charged ions cannot. The probable biological result is reaction of HF within the cell rather than reaction during the process of attacking the cell wall.

Effects of Interhalogens Upon Microorganisms

In principle, much of the discussion of interhalogen effects upon fish is also applicable to microorganisms. The acid and oxidizing characteristics of interhalogen solutions are responsible for effects upon single cell organisms in aqueous systems and the addition of base or reducing compounds effectively interferes with the effects of the solutions upon microorganisms.

Since the interhalogens, as gases, might penetrate soil to a significant extent, effects upon microbial populations in dry soils were studied. We found ClF_3 to be highly destructive to microbial populations in natural soil at concentrations of about 400 ppm for about 30 minutes. After this treatment, bacterial and fungal populations remain at a low level for several days before they eventually begin to increase their numbers and approach normal populations again. In contrast, BrF_5 was relatively ineffective at a comparable concentration and did not cause extensive lethality to organisms in dry soil until the concentration in the atmosphere was raised to 5,000 ppm. This difference may be due to the rapid condensation of BrF_5 on the very high surface area of the powdered soil used in the experimental procedures. It was not possible to maintain experimental concentrations of ClF_5 in air in this series of studies, presumably because of reactions with the soil.

Experiments in which toxic gases are passed through dry soil probably do not represent a situation which may be expected in the field. It is much more likely that microorganisms in soil will be exposed to interhalogens in the form of aqueous solutions formed in the course of decontamination activity or heavy rainfall. In our experiments, passage of solutions of the interhalogens, sodium fluoride and hydrofluoric acid through soils caused little change in soil microbial population.

While toxicity of accidentally released interhalogens to soil microorganisms should be limited, damage to microbial populations of ponds and water courses may be substantial. In aqueous solutions, ClF_3 was lethal to each of four selected species of organisms suspended in distilled water at a concentration of 22.5 µg fluoride per milliliter, over an exposure period of 2 hours. Each organism is quite sensitive to 12.2 µg per ml as well, and below this level, the effect varies (Table II). Of the various organisms, B. subtilis was found to be quite sensitive to experimental manipulation which may have influenced its tolerance of low level exposures. The natural microbial population of river water, after transfer to distilled water, was also heavily affected by ClF_3. When these various solutions were neutralized to pH 6.5 by sodium bicarbonate, there was little or no relief of the lethal effects. Treatment of the solutions with cysteine alone decreased their toxicity slightly, but most of the lethal effect upon specific organisms remained. When a lethal solution of ClF_3 was treated with both cysteine and bicarbonate, however, the lethal effect was lost completely.

The Effect of Aqueous Solutions of BrF_5 Upon Microorganisms

In distilled water, BrF_5 at concentrations above 10.8 µg fluoride per ml was 100% lethal to all species studied. In river water, a concentration of 34.3 micrograms fluoride per ml was necessary to cause complete lethality and no effect could be detected at concentrations below 26 µg/ml. Neutralization of pH to 6.5 resulted in changes ranging from a limited decrease in

TABLE II. Effects of ClF_3 in Aqueous Solution Upon Microorganisms -- 2 Hour Exposure

Organism	Suspending Medium	Concentration in µg F^-/ml	% Survival
A. radiobacter	distilled water	0	100
	"	7.7	100
	"	12.2	1
	"	22.5	0
A. globiformis	distilled water	0	100
	"	7.7	100
	"	12.2	8
	"	22.5	0
B. subtilis	distilled water	0	100
	"	7.7	0
	"	12.2	0
	"	22.5	0
P. fluorescens	distilled water	0	100
	"	7.7	4
	"	12.2	2
	"	22.5	0
River Water Population	distilled water	0	100
	"	6.3	2
		10.0	0

effect upon *B. subtilis* to a complete loss of lethal effect upon *A. radiobacter*. Subsequent addition of cysteine to such neutralized solutions had no effect, or in some cases actually increased lethality. When a more effective buffering system such as $KH_2PO_4 \cdot Na_2HPO_4$ was employed, BrF_5 became innocuous to microorganisms, until the concentration rose to the level at which toxicity of fluoride becomes dominant.

The Effects of Aqueous Solutions of ClF_5 Upon Microorganisms

In the laboratory, ClF_5 solutions containing 12.8 micrograms fluoride per ml were 100% lethal to microorganisms in distilled water and substantial losses occurred at a concentration of 8.6 micrograms fluoride per ml. Elevation of the pH to 6.4 caused some decrease in lethal effect of ClF_5 and the addition of cysteine completely eliminated the lethal action. A sample of the natural microbial population of Mary's River water was completely destroyed at ClF_5 concentrations above 29.6 μg fluoride/ml, and substantial effects were apparent at a concentration of 15.5 μg fluoride per ml. A major factor in the difference in effect between solutions of ClF_5 in river water and in distilled water was clearly the reducing capability of the river water. This function was extensive enough that addition of sodium bicarbonate alone was sufficient to prevent effects of substantial concentrations of ClF_5.

The time required for moderately lethal interhalogen solutions to affect microorganisms appears to be at least 90 minutes. No additional decrease in population was found, even after 24 hours of exposure. Measurable lethality could not be detected after 30 minutes of exposure, and the microbial population of the toxic solution was only 60% depleted at 1 hour. By 90 minutes, the effect had reached a maximum and no further lethality occurred.

In evaluating the effect of interhalogen solutions, it is necessary to consider also the effect of hydrofluoric acid and other inorganic acids upon microorganisms in suspension. As noted previously, fish subjected to solutions of interhalogens and inorganic acids were unable to survive pH levels lower than about 3.5 to 3.9. The relationship of hydrofluoric acid toxicity to the capability of fish for raising pH was shown by experiments. Fish were found to be readily able to raise the pH of most strong inorganic acids to tolerable levels, under the experimental conditions employed, but could raise the pH of HF solutions only with great difficulty. A similar effect can be demonstrated in the response of microorganisms to inorganic acids. There is an abrupt loss of lethal effect as the initial pH to which the organisms are subjected is increased (Table III). Studies with HCl solutions show, quite reasonably, that these points correspond in general with increased capability, at higher pH levels, for neutralizing or buffering the acid to a tolerable hydrogen ion concentration.

TABLE III. Lethality to Microorganisms of HF and HCl Solutions at Various pH Levels and the Effect of Microorganisms Upon pH of HCl Solutions*

	Initial pH	A**	B	C	D	A	B	C	D
		% Lethality				Terminal pH			
HCl	2.8	99.3	98.4	100	100	2.9	3.0	3.0	3.1
	3.0	99.3	90.7	100	100	3.3	3.3	3.3	3.4
	3.2	99.9	86.4	100	97.7	3.6	3.7	3.7	3.9
	3.4	0	0	100	0	6.6	4.2	5.8	6.0
	3.6	0	0	100	0	7.0	6.2	7.0	6.4
	4.0	0	0	100	0		6.1	7.0	6.7
HF	3.16	100	100	100	100				
	3.22	100	100	100	100				
	3.27	100	100	100	100				
	3.50	100	99.8	100	99.7				
	3.59	99.7	99.4	100	98.4				
	3.92	93.3	0.0	100	0.0				
	4.03	0.0	0.0	95	0.0				
	4.47	0.0		62					
	4.72			0.0					

*Exposure period: 2 hours

**Concentration of Organisms:

HF	A	A. radiobacter,	4×10^8
	B	A. globiformis,	4×10^8
	C	B. subtilis,	6×10^5
	D	P. fluorescens,	3×10^8
HCl	A	A. radiobacter,	5×10^8
	B	A.globiformis,	3×10^8.
	C	B. subtilis,	2×10^5.
	D	P. fluorescens,	3.4×10^8.

Effects of Interhalogens Upon Plants

The grossly visible effects of BrF_5, ClF_3 and ClF_5 upon plants were similar, although the concentration of ClF_5 required for effect appeared to be somewhat higher than that of the other agents.

The symptoms of exposure to this series of agents varied from severe burning at high doses to a decrease in growth rate without surface lesions at very low doses. In most cases, the effects seemed confined to the tissues which were actually contacted by the toxic material. In moderate exposures, exposed leaves often wilted and died, but the new shoots emerged and developed without noticeable damage. In some instances of extreme exposure, the stem remained sufficiently viable that new leaf formation began several days after exposure. Grass leaves, which gradually unsheath as they grow were often burned at the exposed tip and healthy on the surface which emerged after exposure.

In every case where visible damage occurred, however, the general vigor of recovering plants appeared attenuated. There is no question that any crop affected by interhalogens would represent an economic loss, and it is highly possible that intoxication at lower levels may result in deficient yield or quality as well.

The experimental studies of plant intoxication were designed for estimation of the lower effective limits of exposure, and this information has been summarized in Table IV. Detailed descriptions of behavior of plants under various exposure conditions have been presented previously (ref. 2).

It is important to recognize that of the biological groups we have observed, plants are the most sensitive indicators of area contamination by inorganic fluoride oxidizing agents. Plants tend to respond to varying levels of toxic attack with corresponding degrees of resulting damage, and suffer immediate destruction only at very high concentrations of corrosive agents. This sensitivity arises from the immobility and large surface area of plants and the absence of such protection as fish and microorganisms are provided by water and soil.

While the injuries observed so far are probably non-specific, the extent of damage resulting from accidental spillage should be easily evaluated, since there should be a drift range beyond which no symptoms occur. Further, most crops of economic concern are replanted yearly, and there is as yet no evidence that subsequent plantings will be affected.

TABLE IV. Effects of Inorganic Fluoride Oxidizing Agents Upon Plants and Seeds

Agent	Age	A*	B**	Remarks
		ppm/minute	ppm/minute	
N_2F_4	seeds	$10^4/60$	$10^5/60$	$>10^5/60$ caused 100% inhibition
	10 day old	$>10^3/30$	$10^4/30$	
	30 day old	ND	ND	
NF_3	seeds	100%/1-6 hrs		
	15 day old	see remarks	see remarks	No symptoms at 10,000 ppm
	30 day old	see remarks	see remarks	No symptoms at 10,000 ppm
OF_2	seeds	ND	ND	
	15 day old	1.5/30	10/30	At low concentration, some internodal lengthening
	30 day old	ND	10/30	
ClF_3	seeds	100/60	130/60	
	15 day old	10/15	15/15	At 10/15, bean and squash not affected
	30 day old	ND	15/15	
ClF_5	seeds	ND	ND	
	15 day old	50/15	ND	Slow onset, peas very sensitive at both ages
	30 day old	ND	50/30	
BrF_5	seeds	ND	100/30	
	15 day old		50/30	Corn, squash, sudan grass sensitive
	30 day old	ND	50/30	

*A--minimum exposure causing detectable damage

**B--minimum exposure causing probable major loss as economic crop

ND--not determined

Effects of Aqueous Interhalogen Solutions on Growing Plants

Irrigation of plants with ClF_3 solutions containing 50 and 100 μg fluoride/ml caused some necrotic damage, but no significant change was found in plant stature or in the fluoride content of the leaves and stems of these plants. A reaction mixture of BrF_5 in water containing 470 μg fluoride/ml caused slight effects on pea, squash and Sudan grass plants within a 2-week observation period. The next section will deal with the attenuating influence of soil upon interhalogen solutions.

SECTION IV

THE INFLUENCE OF SOIL AND WATER ON INTERHALOGEN SOLUTIONS

The general chemical behavior of the inorganic fluoride oxidizing agents has been discussed more or less independently in order to anticipate the nature of the products which will contact and intoxicate organisms in the field. The toxic behavior of accidentally released inorganic fluoride oxidizing agents depends upon their interaction with the non-biological factors of the environment, particularly water and soil.

NF_3, N_2F_4 and OF_2 are unlikely to dissolve appreciably in water in the event of spillage under unconfined conditions because of their low boiling point even though the relatively high molecular weight of the gases relative to air may cause them to stay near the point of release for at least a short period of time. The interhalogens, on the other hand, may easily react with surface water, rain or decontamination washings, after which the products may be carried into water courses directly or by percolation through soil. Consequently, this discussion of the interactions of inorganic fluoride oxidizing agents with soils and water deals almost entirely with the interhalogens.

As previously noted, interhalogen solutions are strongly acidic and possess substantial oxidizing activity. The relationship of these characteristics to lethality and their independence of each other in this respect have been demonstrated with fish and microorganisms and are described elsewhere in this report.

The detrimental biological activity of interhalogen solutions associated with acid effects can be attributed to HF, but the chemical identity of the lethal component (s) among the oxidizing species is as yet uncertain. Experimental comparisons of the hydrogen ion concentration of interhalogen and HF solutions in distilled water and in waters from various sources in nature (Table V) suggest that most of the fluoride of interhalogen solutions is present as HF. The relative capability of waters from various natural sources for buffering of acids is also suggested in Table V although this information is somewhat obscured by inconsistencies in the relation of pH with fluoride concentration, which indicate that ClF_3 and BrF_5 have a lower

TABLE V. Effect of Waters from Various Sources Upon pH of Interhalogen and HF Solutions

Water Type	Fluoride Concentration	pH values of solutions of			
		ClF_3	BrF_5	HF	HF*
Distilled	30 µg/ml	3.37	2.83	3.13	3.12
water	20	3.51	2.90	3.25	3.24
	15	3.62	2.98	3.34	3.32
pH 6.7	10	3.88	3.08	3.47	3.45
	5	4.05	3.22	3.65	3.70
De-chlorinated	30	3.28	2.88	3.58	
tap water	20	3.55	3.08	3.98	
	15	3.84	3.29	4.84	
pH 7.48	10	5.10	3.53	6.20	
	5	6.26	4.20	7.00	
River water	30	3.42	3.05	4.83	
	20	3.73	3.20	6.14	
pH 7.55	15	4.11	3.27	6.50	
	10	3.68	5.74	6.70	
	5	6.15	4.75	7.00	
Seawater	30	3.52	2.96	4.25	
	20	5.25	3.24	5.87	
pH 7.59	15	6.33	3.46	6.10	
	10	6.42	4.29	6.45	
	5	6.88	6.18	6.85	

*Calculated pH of HF solutions on basis of concentration of fluoride
$Ki = 6.9 \times 10^{-4}$

pH than HF itself. It is possible that HCl and HBr may make some slight contribution to the hydrogen ion concentration of the respective interhalogen solutions, but most of the chlorine or bromine is apparently associated with oxidizing compounds.

These data do show, however, that there is little difference in buffering capability between seawater and water from other sources.

Of the various waters, only river water was capable of causing an appreciable decrease in oxidizing activity of interhalogen solutions (Table VI). The low reducing power of seawater is especially interesting in view of its estuarine source where a great deal of suspended organic material might be expected.

TABLE VI. Oxidizing Capability of ClF_3 Solutions Prepared in Waters From Various Sources

μg fluoride/ml	Distilled Water	Dechlorinated Tap Water	River Water	Seawater
	(milliequivalents KI oxidized/liter)			
30	57.5	62.1	33.4	54.5
20	39.6	42.4	23.3	36.2
15	31.5	31.5	16.7	27.8
10	21.6	20.1	11.0	17.2

Interaction Between Soil and Inorganic Fluoride Oxidizing Agents

Exposure of dry soil to dry gases apparently results in little direct reaction. There is no detectable change in soil pH until atmospheric concentrations of interhalogens rise above 10,000 ppm. Undiluted NF_3 and N_2F_4 caused no change in pH of soil.

The effect of soil upon solutions of the various interhalogens is substantial, however. The most dramatic is the loss of oxidizing capability. For example, a ClF_5 solution assayed at 3,170 μg fluoride per ml was found to require 1.54×10^{-2} equivalents of sodium thiosulfate per ml to reduce the iodine it could liberate from potassium iodide. After shaking 25 ml of the solution with 2 g of Woodburn soil, an oxidizing capability of only about 10^{-4} equivalents per ml remained.

The effect of Woodburn soil upon solutions of ClF_3 and of BrF_5 was essentially identical. A Jory type soil, containing more clay, was still more effective in lowering the oxidizing capability of the solutions. Solutions passed through columns of soil in experiments simulating the percolation and subsequent leaching to be expected in the field are also effectively stripped of oxidizing action (Table VII). In both percolation (Table VII) and contact (Table VIII) experiments, substantial amounts of the initial fluoride content of interhalogen solutions remains trapped in soil. Similarly, much of the hydrogen ion of solutions is also retained by soil during percolation.

These effects of soils upon interhalogen solutions are of great importance in the light of findings that treatment of such solutions with buffers and reducing agents renders them nearly harmless. It follows that solutions resulting from water decontamination or rain in the area of interhalogen spillage should not threaten fish and aquatic organisms if the solutions can be passed through soil en route to water catchments. This is apparently true, with certain reservations.

Samples of the various experimental filtrates and distilled water washings were uniformly found to cause some limited mortality to fish at fluoride concentrations several times higher than were necessary before treatment with soil. Also, the time required for effect was greatly lengthened. Since the amount of soil relative to solution was much less than should be encountered in field conditions, it is unlikely that any field interhalogen contamination would prove toxic after washing into soil.

TABLE VII. Characteristics of Interhalogen Solutions After Filtration Through and Elution from A. Woodburn soil and B. Jory Soil

	ml drained from soil	µg F/ml	Total mg Fluoride	pH	Equivalents $Na_2S_2O_3$/ml
300 ml ClF_5 solution added		3170	951	4.0	0.0105
	140	600	84	4.0	0.0
A:					
1st 100 ml washing*	100	900	90	4.6	
2nd " " "		900	90	5.0	
3rd " " "		775	77.5	5.4	
8th " " "		18.5	18.5	5.8	
12th " " "		8.0	8.0	5.9	
	recovery of added fluoride**		570 mg	= 60%	
300 ml ClF_5 solution added		3170	951	4.0	0.0105
	140	435	61	3.5	
B:					
1st 100 ml washing	100	335	33.5	5.0	0.0
2nd " " "		300	30	5.3	
3rd " " "		250	25	5.6	
8th " " "		110	11	6.0	
12th " " "		75	7.5	6.0	
	recovery of added fluoride		266 mg	= 28%	
300 ml ClF_3 solution added		2400	720	3.0	0.019
	140	825	115	3.0	0.0
A:					
1st 100 ml washing	100	1000	100	4.6	
2nd " " "		800	80	5.0	
3rd " " "		600	60	5.2	
4th " " "		400	40	5.3	
8th " " "		60	6	---	
12th " " "		10	1	---	
	recovery of added fluoride		402 mg	= 56%	

continued . . .

TABLE VII. continued . . .

300 ml ClF_3 solution added		2400	720	3.0	0.019
	140	500	70	3.5	
B:					
1st 100 ml washing	100	400	40	4.9	
2nd " " "		275	27.5	5.4	
3rd " " "		170	17	5.7	
8th " " "		80	8	6.0	
12th " " "		55	5.5	6.2	

recovery of added fluoride 226 mg = 31%

---

300 ml BrF_5 solution added		3100	930	2.9	0.03
	140	425	59	4.2	0.0
A:					
1st 100 ml washing	100	900	90	4.0	
2nd " " "		850	85	4.3	
3rd " " "		710	71	4.9	
8th " " "		180	18	5.7	
12th " " "		70	7	5.8	

recovery of added fluoride 492 mg = 52%

---

300 ml BrF_5 solution added		3100	930	2.9	0.03
	140	710	99	2.6	0.0
B:					
1st 100 ml washing	100	330	33	4.6	
2nd " " "		225	22.5	4.9	
3rd " " "		150	150	5.1	
8th " " "		85	8.5	5.5	
12th " " "		75	7.5	5.7	

recovery of added fluoride 250 mg = 27%

---

* distilled water

**includes all washes

TABLE VIII. Characteristics of Interhalogen Solutions After Static Contact With Soils for One Hour

	Grams Soil Contacted	µg F/ml	pH	Relative Oxidizing Capability
HF Solution				
in	None	2700	1.9	±
(Woodburn Soil)	1	1925	1.9	-
	5	1820	2.4	-
	10	1480	3.0	-
	20	975	3.9	-
	30	250	4.1	-
in				
(Jory Soil)	1	1750	2.0	-
	5	1375	2.8	-
	10	1035	3.3	-
	20	325	4.6	-
	30	325	5.3	-
ClF_3 Solution				
in	None	2400	1.5	++++
(Woodburn)	1	1910	1.5	+++
	5	1840	1.8	++
	10	1750	2.2	±
	20	1125	3.4	-
	30	665	3.8	-
in				
(Jory)	1	1910	1.6	++
	5	1620	2.2	±
	10	1160	3.2	-
	20	525	3.8	-
	30	300	3.8	-

continued . . .

TABLE VIII. Continued . . .

ClF_5 Solution

in (Woodburn)	None	2170	1.7	+++
	1	3000	1.7	++
	5	2820	2.3	+
	10	2500	2.8	±
	20	1700	3.9	-
	30	1085	4.2	-
in (Jory)	1	3000	2.0	+
	5	2430	2.5	±
	10	1650	4.0	-
	20	866	4.6	-
	30	500	4.8	-

BrF_5 Solution

in (Woodburn)	None	3100	1.5	++++
	1	2715	1.6	+++
	5	2665	2.1	++
	10	2370	2.7	±
	20	1650	3.7	-
	30	985	4.0	-
in (Jory)	1	2870	1.9	+++
	5	2350	2.4	++
	10	1635	3.9	-
	20	815	4.2	-
	30	400	4.5	-

---

*soil placed in 25 ml of solution in 50 ml plastic centrifuge tube

SECTION V

CONCLUSIONS

The problem of protection against accidentally released inorganic fluoride oxidizing agents obviously extends into the engineering and chemistry of methods for dissipating toxic atmospheres before enough time has elapsed to cause permanent damage. The varied character of these agents, in terms of their toxicity and their tendencies to react in the environment can be appreciated from examination of Table IX. The problem is formidable in the case of OF_2, which is lethal to mammals after 10 minutes of exposure to 15 ppm and causes grossly observable lesions in plants at concentrations of 1.5 ppm over a period of 30 minutes. Because of the relative stability of OF_2, environmental protection seemingly can only be accomplished by eventual dilution of the gas in the atmosphere, with the accepted loss of some finite amount of plant and animal life. Personnel protection in the use of this agent must be absolute; no material of this character can be assigned a minimal acceptable concentration of more than zero, and the nature of the lesions caused by OF_2 preclude therapeutic efforts.

The magnitude of the problem may be perceived by considering the degree of contamination resulting from release of one ton of OF_2. The total volume occupied by one ton of OF_2 after dilution to 1.5 ppm in air is on the order of 2.5×10^8 cubic meters, an amount which would cover about 320 acres to a depth of 100 yards. At the time of release, however, the volume occupied is about 290 cubic meters, assuming no dilution at atmospheric pressure.

A possible productive approach to decontamination of spilled OF_2 may be through the immediate reaction of the spilled gas by reagents distributed through the cloud, at a time when concentration is high enough to permit relatively easy reaction in a limited area. If compounds can be found that will destroy OF_2 and other agents which react with difficulty, they should tend to resist dissipation of a gas cloud, since the concentration gradient of unreacted gas should be inward toward the decontaminant.

TABLE IX. General Index of Toxic Hazards Expected as a Result of Accidental Release of Inorganic Fluoride Oxidizing Agents

	Boiling Point °C	Reactivity	Tendency to Solution in Water	Soil Interaction with Solutions	General Toxicity	Remarks
NF_3	-129	inert	O		±	virtually no effect on plants; no effect on fish or microorganisms; high concentrations cause reversible toxicity in mammals
N_2F_4	- 73	quick decomposition in air if water is present	+		+	limited effects on plants; reaction products relatively harmless to fish. Mammalian toxicity moderate but reversible
OF_2	-145	quite stable--limited hydrolysis	+ (degasses very quickly)	some reduction	>++++	no appreciable microbial or fish effects unless partial pressure remains high. Very high toxicity to plants. Absolutely zero tolerance for mammals; damage irreversible, no successful decontamination
ClF_3	11.75	reacts abruptly with organic matter or water, extensive surface reactions	++++	substantial reduction	++++	quite toxic to plants, high toxicity as aqueous solution to fish and microorganisms, but can be neutralized chemically or by filtration through soil; HF and oxidizing species both cause toxicity
ClF_5	- 13.1	rapid but not explosive reaction with water, dangerous in contact with surface organic material	+++	substantial reduction	+++	same as ClF_3 but to a lesser degree
BrF_5	40.8	violently reactive with organic matter and water, extensive surface reactions	++++	substantial reduction	++++	same as ClF_3, but little apparent effect from oxidizing component

In attempting to combat the effect of interhalogens, a much more encouraging situation exists. These compounds are somewhat less toxic, although plant effects at low concentrations may be severe. More important, the interhalogens react with almost any material that they encounter, a characteristic which can be turned to some utility in depleting the atmosphere of these compounds. For example, immediate generation of high volumes of mist or fog at sites of spillage may reduce the amount of active material present in a very few minutes. If this reaction time can be shortened sufficiently without causing explosive reactions, it may be a means of saving the lives of individuals trapped within the complex where accidental release has occurred. Damage might then be limited to downwind surface organisms.

The reactive aqueous solutions formed must be dealt with as well, for personnel protection and defense of the downstream ecology; but if the waterborne interhalogen reaction products are eluted or percolated through the local soil, almost all biological factors of the environment will probably be protected. A similar defense is likely to prevail in the event of accidental N_2F_4 spillage, and although reactions should be somewhat slower, the toxicity of this agent is much less than that of interhalogens.

Oregon State University is presently engaged in studies directed at the problem of quickly and safely destroying each of the inorganic fluoride oxidizing agents in air, leaving products which may be dealt with on a non-emergency basis. When satisfactory chemical control measures evolve through this effort, application in the field should sharply diminish the potential hazard of accidental release of inorganic fluoride oxidizing agents.

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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Oregon State University Radiation Center Corvallis, Oregon 97331	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP N/A

3. REPORT TITLE

STUDIES ON ENVIRONMENTAL POLLUTION BY MISSILE PROPELLANTS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report, May 1964 - June 1967

5. AUTHOR(S) *(First name, middle initial, last name)*

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6. REPORT DATE February 1969	7a. TOTAL NO. OF PAGES 28	7b. NO. OF REFS 3

8a. CONTRACT OR GRANT NO. AF33(615)-1767	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 6302 c. Task No. 630204 d. Work Unit No. 6302 04 001	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* AMRL-TR-68-85

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Aerospace Medical Research Laboratory Aerospace Medical Div.,Air Force Systems Command, Wright-Patterson AFB,OH 45433

13. ABSTRACT

The effects of single experimental exposures of plants, fish and microorganisms to members of a group of inorganic fluoride oxidizing agents have been summarized. The information obtained has enabled estimation of the damage to be expected as a result of single accidental exposures in the field. These agents--nitrogen trifluoride (NF_3), tetrafluorohydrazine (N_2F_4), oxygen difluoride (OF_2), chlorine trifluoride (ClF_3), bromine pentafluoride (BrF_5), and chlorine pentafluoride (ClF_5)--vary in chemical behavior and biological effects. NF_3 is relatively innocuous; OF_2 must be avoided absolutely by animals and plants, and both are quite stable chemically. The interhalogens react readily in contact with environmental constituents, and while destructive at the site of initial contact, they are self limiting in effect. N_2F_4 also reacts easily, but should cause only moderate damage. Plant injury in all cases would probably be limited to the currently growing crop, with little possibility of carry-over effects in soil.

DD FORM 1 NOV 65 1473

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nitrogen trifluoride, NF_3						
Tetrafluorohydrazine, N_2F_4						
Oxygen difluoride, CF_2						
Chlorine Trifluoride, ClF_3						
Chlorine pentafluoride, ClF_5						
Bromine pentafluoride, BrF_5						
Effects on plants						
Effects on fish						
Effects on bacteria						
Pollution Index						

Security Classification